

(12) UK Patent Application (19) GB (11) 2 178 048 A

(43) Application published 4 Feb 1987

(21) Application No 8617468

(22) Date of filing 17 Jul 1986

(30) Priority data

(31) 60/157912
60/157913

(32) 17 Jul 1985
17 Jul 1985

(33) JP

(51) INT CL⁴

C08F 220/18 2/14 218/10 263/02 267/06 G03G 9/12 //
(C08F 220/18 218:12 220:18 220:06 222:02 224:00)
(C08F 218/10 218:12 220:18 220:06 222:02 224:00)

(52) Domestic classification (Edition I):

C3P 156 158 160 210 212 220 222 234 256 302 304 310
314 322 EG FE
G2C TA
U1S 2243 C3P G2C

(71) Applicant

Ricoh Co. Ltd.,

(Incorporated in Japan),

No. 3-6 Nakamagome 1-chome, Ohta-ku, Tokyo, Japan

(56) Documents cited

None

(58) Field of search

C3P

Selected US specifications from IPC sub-class C08F

(72) Inventors

Kazuo Tsubuko,
Shinichi Kuramoto,
Kayoko Nagai,
Makoto Okawara,
Hajime Takanashi

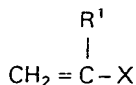
(74) Agent and/or Address for Service

Marks & Clerk, 57-60 Lincoln's Inn Fields,
London WC2A 3LS

(54) Non-aqueous resin dispersing and electrophotographic developers containing them

(57) A non-aqueous resin dispersion, suitable for use in the formation of a liquid electrophotographic developer, is prepared by copolymerising in an aliphatic hydrocarbon solvent

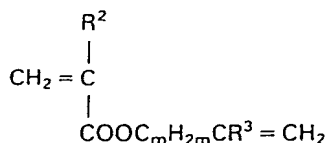
(i) a monomer A of the formula:



(II)

(in which R¹ is a hydrogen atom or a methyl group and X is a group -COOC_nH_{2n+1}, or -OCOC_nH_{2n-1}) in which *n* is an integer from 6 to 20);

(ii) a monomer B of the formula:



(III)

(in which R² and R³ are each a hydrogen atom or a methyl group and *m* is an integer of from 1 to 20); and

(iii) an ethylenically unsaturated monomer C containing a carboxyl or glycidyl group.

Another monomer D (e.g. methyl methacrylate) may be graft polymerized onto the copolymer of A, B and C.

GB 2 178 048 A

Case 3548
PCT

SPECIFICATION

Non-aqueous resin dispersions and electrophotographic developers containing them

5 The present invention relates to non-aqueous resin dispersions which may be used in the formulation of liquid developers for electrostatic photography, paints, printing inks, adhesives and the like. 5

The resin dispersions used in the formation of liquid developers for electrostatic photography, paints, inks and the like, have normally been prepared by dispersing separately prepared resins, such as alkylphenol resins, rosin-modified phenol resins, rosin-modified alkyd resins and maleic resins, in an appropriate organic solvent, i.e. a petroleum aliphatic hydrocarbon or halogenated aliphatic hydrocarbon solvent in the case of developers or an aromatic hydrocarbon solvent in the case of paints or inks. 10

Resin dispersions of this sort should (i) have appropriate viscosity and fluidity, (ii) have good dispersion stability to pigments, (iii) give a coated film which is lustrous and has good adhesive strength, and (iv) give a coated film which dries quickly. However, conventional resin dispersions cannot generally completely satisfy these requirements. 15

In particular, the toner in a conventional liquid developer for electrostatic photography has the problem that although said toner normally functions to cause electrophoresis in response to the electric charge of an electrostatic latent image formed on the surface of an electrophotographic sensitive material or electrostatic recording material and form an image attached to that portion in a development step, the resin and polarity control agent present in the developer tend to diffuse in the carrier liquid with the lapse of time to cause aggregation and make the polarity indistinct so as to markedly reduce image quality, in particular image density. Further, since the adhesive strength of the toner (namely, fixing strength of the image) is weak, the resulting image can be erased with an eraser. In addition when such developers are used for colour electrophotography, four colours, such as yellow, red, blue and black, cannot overlap uniformly due to lack of transparency of the toner, thereby making faithful colour regeneration impossible. Finally, when an image is formed on a zinc oxide sensitive paper and offset printing is effected using this as an offset master, not many durably printed sheets can be obtained and printing is not stable. 20 25

It is an object of the invention to provide a resin which has good dispersibility for pigments and the like and also has good electric charge control and fixativity when used as electrophotographic toner, paint and printing ink, or a dispersion containing said resin. 30

In particular, it is an object of the invention to provide a liquid developer for electrostatic photography having improved storage stability and adhesive strength of the toner, which is superior in gradient, can form a high quality image, is difficult to erase with an eraser, can give improved colour reproduction in colour electrophotography and has improved printing durability and gives rise to less unstable printing. 35

According to the invention there is provided a non-aqueous resin dispersion obtained by copolymerizing, in the presence of a polymerization initiator in an aliphatic hydrocarbon solvent.

(i) a monomer A of the formula:



(in which R¹ is a hydrogen atom or a methyl group and X is a group -COOC_nH_{2n+1} or -OCOC_nH_{2n+1}) in which n is an integer of from 6 to 20); 45

(ii) a monomer B of the formula:



(in which R² and R³ are each a hydrogen atom or a methyl group and m is an integer from 1 to 20); and 55

(iii) an ethylenically unsaturated monomer C containing a carboxyl group or a glycidyl group.

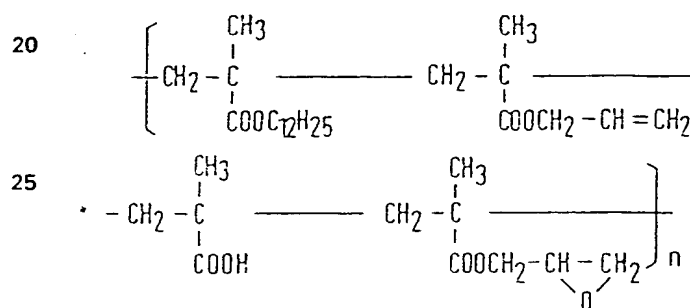
The invention also provides a liquid developer for electrostatic photography containing a non-aqueous resin dispersion obtained as defined above.

We have investigated the desirable properties of a resin (polymer) for achieving the above objectives, and have come to various conclusions. Thus, the polymer should (1) contain a solvation component present in the polymer and the polymer should have uniform graft points; (2) the polymer should contain a crosslinking monomer component that does not cause a too rapid crosslinking reaction; (3) the polymer should contain a monomer component that causes a copolymerization reaction and a crosslinking reaction separately; (4) the polymer should have an affinity for pigments; (5) the polymer should not dissolve in a non-aqueous solvent 60 65

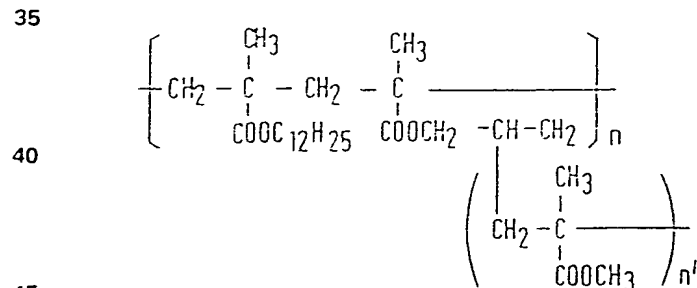
but merely disperse in such non-aqueous solvent; (6) the polymer should be structured to introduce a polar group for dispersing pigments; and (7) the polymer should contain a polar group for raising its adhesive strength. As a result of the investigation of various polymers from these viewpoints we have found that a polymer obtained by copolymerizing monomer A, which has a solvation effect before and after polymerization, monomer B, which can become a graft point or crosslinking component after polymerization, and monomer C having a carboxyl group or a glycidyl group gives good results as does a polymer obtained by further copolymerizing the resultant copolymer with a monomer which is not soluble in a non-aqueous solvent after polymerization (monomer D).

The resin dispersions according to the present invention can suitably be prepared by polymerizing a system containing monomer A, monomer B and monomer C at a temperature of about 60-120°C in the presence of a polymerization initiator which can initiate polymerization at relatively low temperature, such as azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO) or the like, in an aliphatic hydrocarbon (for instance, a solvent comprising a petroleum aliphatic hydrocarbon and/or a halogenated aliphatic hydrocarbon). The polymerization reaction is a conventional one.

By way of Example, copolymerization using lauryl methacrylate as monomer A, allyl methacrylate as monomer B, and a mixture of methacrylic and glycidyl methacrylate as monomer C gives a copolymer (E) having the schematic formula:



Subsequent polymerization, using methyl methacrylate (MMA) as monomer D, gives a copolymer containing groups of the formula:



As shown above, the ideal is to graft copolymerize the MMA (monomer D) with the copolymer E.

Alternatively, however monomer D may be homopolymerized and then grafted to copolymer E for example by mechanically mixing the homopolymer with copolymer E or by applying ultrasonic waves to a mixture of the homopolymer and copolymer E.

As noted above, monomer A is one which can become a solvation component even after polymerization, and specific examples of monomer A are lauryl methacrylate, lauryl acrylate, stearyl methacrylate, stearyl acrylate, 2-ethyl hexyl methacrylate, 2-ethyl hexyl acrylate, dodecyl methacrylate, m dodecyl acrylate, hexyl methacrylate, hexyl acrylate, octyl methacrylate, octyl acrylate, cetyl methacrylate, cetyl acrylate, vinyl laurate, vinyl stearate, nonyl methacrylate, nonyl acrylate, decyl methacrylate, decyl acrylate, cyclohexyl methacrylate and cyclohexyl acrylate.

Monomer B is one which can provide a graft point or crosslinking component after polymerization.

Specific examples of monomer B are listed in Table 1 below.

TABLE 1

Monomers B of formula II.

5	Monomer No.	R ²	R ³	m	5
	B-1	H	H	1	
	B-2	-CH ₃	H	2	
10	B-3	H	-CH ₃	3	10
	B-4	-CH ₃	H	4	
15	B-5	-CH ₃	H	5	15
	B-6	H	H	8	
	B-7	H	-CH ₃	8	
20	B-8	H	H	12	20
	B-9	-CH ₃	H	15	
25	B-10	H	-CH ₃	20	25

Monomer C is a polymerizable monomer having a polar group (a carboxyl or glycidyl group) and is a component which donates an electric charge to a polymer and adsorbs well on the surface of a pigment in a non-aqueous solvent, thereby contributing to dispersibility, adhesiveness and fixativity.

30 Examples of polymerizable monomers C having a carboxyl group include ethylenically unsaturated acids such as acrylic acid, methacrylic acid, itaconic acid, maleic acid and fumaric acid. Examples of monomers C having a glycidyl group include glycidyl acrylate, glycidyl methacrylate, glycidyl propyl methacrylate, glycidyl propyl acrylate, glycidyl butyl acrylate and glycidyl butyl methacrylate.

35 Monomer D is a component which forms fine particles in a non-aqueous dispersion and promote film formability. Specific examples of monomers D are methyl methacrylate, methyl acrylate, ethyl acrylate, ethyl methacrylate, propyl methacrylate, propyl acrylate, n-butyl methacrylate, iso-butyl methacrylate, vinyl acetate, vinyl toluene, styrene, p-chlorostyrene, divinylbenzene, diethylene glycol, dimethacrylate, tri-methylolpropane trimethacrylate, dimethylamino ethylmethacrylate, acrylonitrile, vinylpyrrolidone, vinylpyridine and dimethylaminomethyl methacrylate.

40 The weight ratio of monomer A/monomer B/monomer C is suitably 50-95/1-25/1-25. The weight ratio of the copolymer (E), comprising monomer A, monomer B and monomer C, to monomer D is suitably about 50-95/5-50.

As occasion demands, a suitable amount of another polymerizable monomer may be added to monomer A, monomer B, monomer C or monomer D for copolymerization.

45 Examples of such other polymerizable monomers include styrene, vinyl toluene, nitrostyrene, vinyl acetate, vinylpyrrolidone, dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, diethylaminoethyl methacrylate and diethylaminoethyl acrylate.

It is also possible, during the course of preparation of the dispersion, to add fine silica particles or a wax or a polyolefin having a softening point of about 60-130°C.

50 When using fine silica particles, the resin is believed to be obtained in a state such that fine silica particles are incorporated in its crosslinked structure (network structure). In this instance, silica per se naturally has no possibility of undergoing any physical change such as resolution or the like in the course of reaction. At any rate, when silica is used, dispersion stability can be further improved because the specific gravity of silica is closely akin to that of an aliphatic hydrocarbon (dispersion medium) and gelation of the resin can be prevented.

55 When using a wax or polyolefin, which is dissolved in the reaction system by heating in the course of polymerization reaction but separates out in the form of fine particles on cooling after the completion of polymerization, the resin is believed to be adsorbed on the fine polymer particles. A wax or polyethylene serves not only to improve dispersion stability, because it has a specific gravity closely akin to that of a dispersion medium, prevents gelation of the resin and further has a molecular structure similar to that of the dispersion medium, but also serves to improve adhesiveness because it has a low softening point. The amount of silica, wax or polyolefin added is suitably about 5-50 parts by weight per 100 parts by weight of resin.

60 Specific examples of commercially available waxes and polyolefins having a softening point of 60-130°C are as shown below.

65

Examples of polyethylenes

	Maker	Trade name	Softening point (°C)	
5	Union Carbide (U.S.A.)	DYNI	102	5
		DYNF	102	
10	Monsant (U.S.A.)	DYNH	102	10
		DYNJ	102	
		DYNK	102	
		ORLIZON 805	116	
		ORLIZON 705	116	
		ORLIZON 50	126	
15	Philips (U.S.A.)	MARLEX 1005	95	15
	Du Pont (U.S.A.)	ALATHON 3	103	
20		ALATHON 10	96	20
		ALATHON 12	84	
		ALATHON 14	80	
		ALATHON 16	95	
		ALATHON 20	86	
		ALATHON 22	84	
25	Allied Chemical (U.S.A.)	ALATHON 25	96	25
		AC-POLYETHYLENE 1702	98	
		AC-POLYETHYLENE 6 & 6A	102	
		AC-POLYETHYLENE 615	105	
30	Sanyo Kasei	Sun Wax 131-P	108	30
		Sun Wax 151-P	107	
		Sun Wax 161-P	111	
		Sun Wax 165-P	107	
		Sun Wax 171-P	105	
		Sun Wax E-200	95	

Examples of waxes (Paraffin Waxes)

	Maker	Trade name	Softening point (°C)	
35	Junsei Kagaku Kobayashi Kako	Paraffin Wax	60-98	35
		Bees Wax	65	
		Cetanol	80	
		Bees Wax	110	
40	Nagai Kako Seietsu Kagaku	Furosén	110	40

Polymerization catalysis, other than AIBN and BPO, which may be used include phenylazotriphenyl methane, laurylperoxide, di-t-butylperoxide, t-butyl peroxide and cumene hydroperoxide.

- 45 The aliphatic hydrocarbon solvents used in the present invention includes petroleum type aliphatic hydrocarbons or halogenated aliphatic hydrocarbons such as kerosene, ligroin, n-hexane, n-heptane, n-octane, i-octane, i-dodecane (commercially available examples of which hydrocarbons include "Isopar" H, G, L, K; Naphtha No. 6; "Solvesso" 100 and the like produced by Exxon Corp.). carbon tetrachloride and per-fluoroethylene. Aromatic solvents such as toluene and xylene may be added to small amounts to these
- 50 aliphatic solvents.

In the present invention, polymer particles having a particle diameter of about 0.1-5 μm may be used effectively for paints, printing inks and the like because the particles have good separation stability and adhesive strength between molecules.

- 55 A liquid developer containing the thus obtained copolymer will generally be prepared by mixing 1 part by weight of a colourant with 0.3 - 3 parts by weight of the copolymer; fully dispersing the resultant mixture in the presence of 10-20 parts by weight of petroleum type aliphatic hydrocarbon or a halogenated aliphatic hydrocarbon carrier liquid by means of an attritor, ball mill, KD-mill or the like to produce a concentrated toner; and then diluting the concentrate 5-10 times with a solvent of the same kind.

- 60 In this case, the copolymer dispersion (resin dispersion) obtained as described above may be used, as it stands, to provide copolymer and solvent. It is also possible to add a polarity controller such as a resin other than the copolymer, a metallic soap, lecithin, linseed oil, a higher fatty acid or the like as occasion demands when preparing the concentrated toner. There is however no special necessity to add a polarity controller because the resin of the present invention has a strong polarity and has good dispersion stability.

- 65 As colorants, there may be used conventional inorganic or organic pigments, but colorants prepared by the flushing method are desirably used because pigment particles are dispersed to the extent of primary particles

and so characteristics such as gradient, resolving power and image density are further improved.

- The flushing method for preparing pigments comprises placing a pigment or its hydrated paste together with a resin solution into a kneader (a flusher); mixing so that water present around the pigment is replaced by the resin solution; removing the resultant mixture from the kneader to remove the water phase; drying the resin solution in which the pigment has dispersed to remove the solvent; and thereafter grinding the resultant mass to give a "flushed colorant". The water or solvent may be removed with stirring under reduced pressure. Since a dye, when kneaded with water and used as a slurry be removed with stirring under reduced pressure. Since a dye, when kneaded with water and used as a slurry, can give the substantially same results as does a pigment in the flushing treatment, it is possible to employ a dye which has been subjected to flushing as the toner component. The dye (or pigment)/resin ratio to be used in flushing is suitably 10-60 parts by weight of dye (or pigment) per 100 parts by weight of resin. It is especially useful that the flushing treatment is conducted in the presence of humic acid, humic acid salts (e.g. the sodium or ammonium salts) or a derivative of humic acid. The amounts of humic acid added is suitably about 0.1-30 wt.% of the hydrated dye (or pigment) liquid.
- Suitable resins for use in a flushing treatment include polyolefins, polyolefinvinyl acetate copolymers or modified resins derived therefrom and polyethylene waxes having a softening point of about 50-140°C. Examples of such resins are listed below. In this connection, needless to say that the abovementioned waxes (polyethylene waxes) or polyolefins having a softening point of 60-130°C may also be used for flushing.

20				20
	Maker	Trade name	Softening point °C	
	Eastman Chemical	N-10	111	
25		N-11	108	25
		N-12	113	
		N-14	106	
30		N-34	103	30
		N-45	118	
35		C-10	104	35
		C-13	110	
		C-15	102	
40		C-16	106	40
		E-10	106	
45		E-11	106	45
		E-12	112	
		E-14	104	
50		E-15	100	50
	Mitsui Sekiyu	110P	100	
55	Kagaku	220P	113	55
		220MP	113	
		3200MP	114	
60		210MP	120	60
		4202E	108	
65		4053E	11	65

	Maker	Trade name	Softening point °C	
	Eastman Chemical	N-10	111	
	BASF	OA Wax	93-96	
5	Maker	Trade name	Softening point °C	5
	Petrolite	BARECO 500	86	
10		BARECO 655	103	10
		BARECO 1000	113	
		E 730	93	
15		E 2018	117	15
		E 2020	117	
20		E 1040	105	20
		PETRONABE C	90.5	
		PETRONABA C-36	90.5	
25		PETRONABA C-400	104.5	25
		PETRONABA C-7500	97.8	
30	HEST	PE 520	118-123	30
		PED 121	113-118	
		PED 136	107-112	
35		PED 153	115-120	35
		PED 521	103-108	
40		PED 522	100-105	40
		PED 534	98-105	

45 As the aforesaid other resins that can be added to the developer, there may be enumerated natural resins such as acrylic resins, estergums, hardened rosin and the like, and natural resin-modified maleic resins, phenol resins and pentaerythritol resins. 45

In the case of the liquid developers according to the invention, it is desirable to incorporate (disperse) solid particles having a particle diameter of 1-20 μm therein to improve the image qualities, in particular sharpness and resolving power. As specific examples of such solid particles, there may be mentioned resin particles (for instance, homopolymers of methyl methacrylates such as BR 89, BR 85 and Mitsubishi DIANAL) and in-organic substances (for instance, glass, silica, titanium oxide). Suitably such solid particles are present in amounts of 0.05-5 parts by weight per 100 parts by weight of the total liquid developer (other than such solid particles). 50

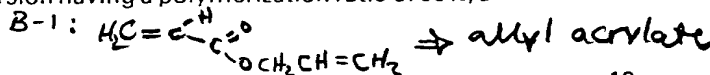
55 The thus obtained liquid developer of the present invention was confirmed to have good transferability and good fixativity on a transfer paper when transferring a toner image obtained by developing an electrostatic latent image onto a transfer paper. The developer was found to give a high image density and high fixativity and further to have good durability and preservability. 55

The developer is also suitably used for offset printing, press transferring, magnetic transferring or the like, not to mention as a developer for general electrophotography. 60

In order that the invention may be well understood the following examples are given by way of illustration only. In the examples all parts are by weight unless otherwise stated.

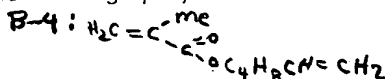
EXAMPLE 1

500 g of kerosene were placed in a 3.0 litre flask equipped with a stirrer, a thermometer, a cooling pipe and a dropping funnel, and were heated to 80°C. A monomer solution, comprising 100 g of lauryl acrylate (monomer A), 50 g of monomer B-1, 10 g of methacrylic acid (monomer C) and 5 g of azobisisobutyronitrile, was added dropwise to the flask with stirring for 2 hours. Thereafter, the resultant mixture was subjected to 4 hours' polymerization reaction at 80°C to give a resin dispersion having a polymerization ratio of 95%, a viscosity of 180 cp and particle diameter of 0.05-0.15 µm.



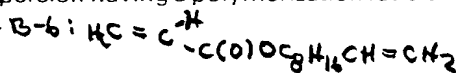
EXAMPLE 2

400 g of n-hexane was placed in the flask used in Example 1, and was heated to 90°C. A monomer solution, comprising 95 g of 2-ethylhexyl methacrylate (monomer A), 25 g of monomer B-4, 10 g of glycidyl propyl acrylate (monomer C), 5 g of acrylic acid (monomer C) and 2 g of azobisisobutyronitrile, was added dropwise to the flask with stirring for 1 hour. Thereafter, the resultant mixture was subjected to 6 hours' polymerization reaction at 90°C to give a resin dispersion having a polymerization ratio of 98.3%, a viscosity of 260 cp and a particle diameter of 0.08-0.24 µm.



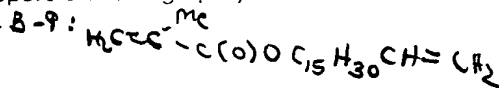
EXAMPLE 3

400 g of Isopar G were placed in the same flask as used in Example 1, and were heated to 90°C. A monomer solution, comprising 200 g of cyclohexyl acrylate (monomer A), 10 g of monomer B-6, 5 g of methacrylic acid (monomer C), 10 g of glycidyl methacrylate (monomer C) and 3 g of benzoyl peroxide, was added to the flask with stirring. The resultant mixture was subjected to 4 hours' polymerization reaction at 90°C. Thereafter, 0.1 g of vinyl pyridine was added thereto, and the reaction mixture was subjected to 10 hours' esterification reaction at 80°C to give a resin dispersion having a polymerization ratio of 96.6%, a viscosity of 280 cp and a particle diameter of 0.10-0.32 µm.



EXAMPLE 4

200 g of Isopar H and 50 g of polyethylene (AC Polyethylene 1106 produced by Allied Chemical) were placed in the flask used in Example 1, and were heated to 90°C to dissolve the polyethylene. A monomer solution, comprising 100 g of stearyl methacrylate (monomer A), 200 g of monomer B-9, 1 g of acrylic acid (monomer C), 8 g of glycidyl acrylate (monomer C) and 10 g of azobisisobutyronitrile, was added dropwise to the flask for 2 hours by means of the dropping funnel, and the mixture was then subjected to 6 hours' polymerization reaction with stirring at 90°C. Then, there were added to the resultant mixture 100 g of methyl methacrylate (monomer D) and 5 g of t-butyl peroxide, and the resultant reaction mixture was subjected to a further 6 hours' polymerization reaction with stirring at 130°C, to give a resin dispersion having a polymerization ratio of 98.0%, a viscosity of 290 cp. and a particle diameter of 0.06-0.23 µm.



EXAMPLE 5-10

Resin dispersions were obtained by using monomers A, B, C and D as shown in Table 2 and following the procedure of Example 1 or Example 4.

Example	Monomer A	Monomer B	Monomer C	Monomer D	Polymerization ratio (%)	Viscosity (c)	Particle diameter (μm)
5	Lauryl methacrylate 100g	B-2 8g	Methacrylic acid 3g Glycidyl acrylate 3g	Vinyl acetate 50g	96.4	102	0.05 -0.15
6	Lauryl methacrylate 100g	B-4 8g	Methacrylic acid 3g Glycidyl acrylate 3g	Ethyl acrylate 50g	95.3	260	0.02 -0.10
7	Lauryl methacrylate 100g	B-6 5g	Methacrylic acid 3g Glycidyl acrylate 3g	Dimethylaminoethyl methacrylate 30g	98.3	185	0.10 -0.20
8	Stearyl methacrylate 100g	B-8 10g	Acrylic acid 5g Glycidyl acrylate 3g	Methyl methacrylate 30g	91.4	266	0.1 -0.15
9	Stearyl methacrylate 100g	B-1 10g	Acrylic acid 5g	Methyl methacrylate 30g	92.5	290	0.05 0.20
10	Stearyl methacrylate 100g	B-3 10g	Glycidyl propyl methacrylate 10g		98.5	350	0.15 0.45

EXAMPLE 11

5	Carbon Black (No.44 produced by Mitsubishi Carbon Co. Ltd)	10 g	5
	Resin dispersion prepared in Example 1	50 g	
	Kerosene	100 g	
10	The above components were dispersed in a ball mill for 20 hours to give a concentrated toner having a viscosity of 42.0 cp. 10 g of the toner were dispersed in 1 litre of kerosene to give a liquid developer for electrostatic photography.		
15	The developer was placed in a commercially available copying machine for electrostatic photography, and copying was effected using zinc oxide sensitive papers to thereby obtain a great number of good copies having an image density of 1.40, a gradient of 10 and an image fixativity of 86.0%. [The image fixativity (%) was calculated from the formula $Y/X \times 100$ (wherein, X represents the image density at an early stage of copying, and Y represents the image density after 5-reciprocating erasing motions using an erasing tester)].		

EXAMPLE 12

20	Carbon Black (Rarven 14 produced by Columbia Carbon Co. Ltd.)	15 g	20
25	Resin dispersion prepared in Example 2	100 g	25
	Isopar G	100 g	

30	The above components were dispersed as described in Example 11 to prepare a concentrated toner. 100 g of the toner was dispersed in 1 litre of Isopar H to prepare a liquid developer for electrostatic photography. The developer was placed in a copying machine for electrostatic photography (Ricopy 5700 produced by Ricoh Co. Ltd) to obtain a great number of good copies having an image density of 1.38, an image fixativity of 88.3% and a gradient of 11. Copying was made on a printing master, and this master was subjected to printing to find that 10,000 sheets could be printed stably.		
----	---	--	--

EXAMPLE 13

40	Flushed colorant comprising 3 parts of phtahlocyanine blue and 7 parts of ethylene-vinyl acetate copolymer (Everflex 210)	100 g	40
	Resin dispersion prepared in Example 4	70 g	
	Kerosene	100 g	

45	The above components were dispersed and diluted as described in Example to prepare a liquid developer for colour electrostatic photography. The viscosity of the concentrated toner was 120 cp. Then, the developer was placed in a commercially available copying machine for colour electrophotography, and colour copying was made on a commercially available zinc oxide sensitive paper, thereby forming a clear-cut colour image.		
50	When copying was made using a copying machine for electrophotography (Ricopy DF 1800R produced by Ricoh Co. Ltd.), furthermore, there was obtained a blue copy having a gradient of 12.		

EXAMPLE 14

55	Carbon Black (MA-11 produced by Mitsubishi Carbon Co. Ltd)	20 g	55
	Resin dispersion prepared in Example 5	130 g	
	Isopar H	100 g	

60	The above components were dispersed and diluted as described in Example 11 to prepare a liquid developer for electrostatic photography. The viscosity of the concentrated toner was 120 cp. Copying was effected following the procedure of Example 11, to give copies having an image density of 1.3 g and an image fixativity of 84.1%. The concentrated toner was stored at room temperature for 3 months and was found to		
65	have a viscosity of 124 cp and very little precipitate. When copying was carried out using this toner, there was		

obtained a copy having an image density of 1.30 and an image fixativity of 85%.

EXAMPLE 15

5	Flushed colorant comprising 4.5 parts of Benzidine Yellow and 5.5 parts of Epolene E-15 (polyethylene)	100 g	5
	Resin dispersion prepared in Example 6	300 g	
10	Isopar H	300 g	10

The above components were dispersed in a KD-mill for 10 hours to prepare a concentrated toner. 100 g of the toner were dispersed in 1 litre of Isopar H to prepare a colour liquid developer for electrophotography. Copying was effected using this developer by means of a copying machine for electrophotography (Ricopy DT 1800R produced by Ricoh Co. Ltd.) to obtain a great number of good copies having a gradient of 12, an image fixativity of 88.0 % and a resolving power of 10 lines/mm.

EXAMPLE 16

20	Flushed colorant comprising 4 parts of Carbon Black (No. 44 produced by Mitsubishi Co. Ltd.), 6 parts of polyethylene (Sunwax 171-P) and 0.5 parts of humic acid	100 g	20
25	Resin dispersion prepared in Example 7	100 g	25
	Isopar G	300 g	

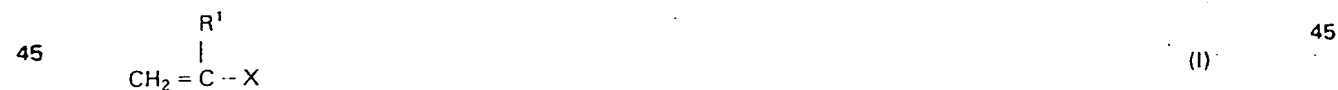
The above components were dispersed in an attritor for 4 hours to prepare a concentrated toner. 1.0 g of DIANAL BR-85 (having an average particle diameter of 13 μ m) was added thereto and stirred. 100 g of the resultant dispersion was dispersed in 1 litre of Isopar G to give a liquid developer for electrophotography.

Copying was effected using this liquid developer and by means of an electrostatic copying machine (Ricopy DT5700 produced by Ricoh Co. Ltd.), obtaining a high quality image having an image density of 1.44, and image fixativity of 86.4 %, a gradient of 10 and a superior sharpness.

As is evident from the above Examples, the resin dispersion according to the present invention is superior in dispersibility and adhesiveness, and is especially useful for liquid developers.

CLAIMS

- 40 1. A non-aqueous resin dispersion obtained by copolymerising, in the presence of a polymerization initiator in an aliphatic hydrocarbon solvent,
- (i) a monomer A of the formula:



(in which R^1 is a hydrogen atom or a methyl group and X is a group $-COC_nH_{2n-1}$, or $-OCOC_nH_{2n+1}$ in which n is an integer from 6 to 20);

- (ii) a monomer B of the formula:



60 (in which R^2 and R^3 are each a hydrogen atom or a methyl group and m is an integer of from 1 to 20); and

(iii) an ethylenically unsaturated monomer C containing a carboxyl or glycidyl group.

2. A dispersion as claimed in Claim 1, wherein the weight ratio of monomer A: monomer B: monomer C is 50-95:1-25:1-25.

3. A resin dispersion as claimed in Claim 1, or Claim 2 in which the copolymer of monomers A, B and C is subsequently copolymerized with a monomer D.

4. A dispersion as claimed in Claim 3, wherein the weight ratio of the copolymer of monomers A, B and C is the monomer D is 50-95: 5-50.

5. A dispersion as claimed in Claim 3 or Claim 4 wherein monomer D is methyl methacrylate, methyl acrylate, ethyl acrylate, ethyl methacrylate, propyl methacrylate, propyl acrylate, n-butyl methacrylate, iso-butyl methacrylate, vinyl acetate, vinyl toluene, styrene, p-chlorostyrene, divinylbenzene, diethylene glycol, dimethacrylate, trimethylolpropane trimethacrylate, dimethylamino ethylmethacrylate, acrylonitrile, vinylpyrrolidone, vinylpyridine or dimethylaminomethyl methacrylate.

6. A dispersion as claimed in any one of the preceding claims also containing silica, a wax or a polyolefin.

7. A dispersion as claimed in claim 1 substantially as hereinbefore described with reference to Example 1-10.

8. A liquid developer for electrostatic photography containing a dispersion as claimed in any one of the preceding claims.

9. A developer as claimed in claim 8 substantially as hereinbefore described with reference to any of Examples 11-16.

Printed for Her Majesty's Stationery Office by Croydon Printing Company (UK) Ltd, 12/86, D8817356.
Published by The Patent Office, 25 Southampton Buildings, London WC2A 1AY, from which copies may be obtained.